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Ozone Production from Irradiation of Acetylene/Chlorine Mixtures in Air

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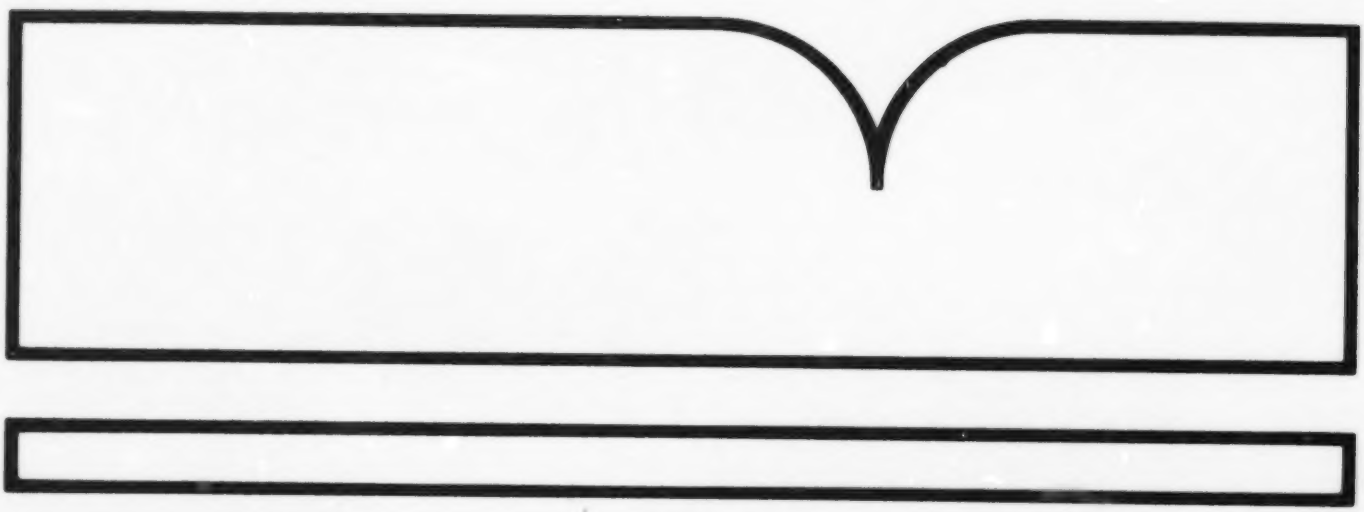

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16. ABSTRACT

The reaction of chlorine radicals with acetylene in air in the absence of oxides of nitrogen result in the formation of ozone. No ozone is observed when chlorine radicals react with methylacetylene or ethylacetylene under similar conditions. Formyl chloride is observed in all systems. A mechanism is proposed for the major products observed in the acetylene reaction. The addition of chlorine to acetylene followed by molecular oxygen addition results in the formation of the peroxychloroethylene radical. A possible explanation for O_3 production is elimination of an oxygen atom from such radicals with excess energy, followed by reaction with molecular oxygen. In the case of substituted acetylenes the larger radicals formed may be able to dissipate the excess energy. Without the formation of atomic oxygen, ozone is not formed. This study demonstrates another mechanism through which ozone may be formed in addition to NO_2 photolysis. More work is required to more fully clarify the mechanism for O_3 production.

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Ozone formation from Irradiation of Acetylene/Chlorine Mixtures in Air

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While studying the photooxidation of acetylene in the presence of chlorine atoms, an unexpected product, ozone, was observed. This occurred at short irradiation times. The system contained only acetylene, chlorine, and tank air devoid of any oxides of nitrogen. Under tropospheric conditions the usual source of ozone is through the photolysis of nitrogen dioxide in the presence of volatile organic hydrocarbons (VOCs).

When chlorine atoms are used in the presence of VOCs, the chlorine radicals are thought to react in a manner similar to OH radicals. They abstract a labile hydrogen from a paraffin or an aldehyde or add to a double or triple bond. An example of this is the facile manner in which peroxyacetyl nitrate is produced, from acetaldehyde, chlorine, and nitrogen oxides.[1] However, no free atomic oxygen is expected to be produced. To our knowledge, this is the first time that ozone has been observed as a product from the photooxidation of acetylene in the presence of chlorine atoms in the absence of oxides of nitrogen.

Experimental

The reactions of chlorine radicals with acetylene, methylacetylene, and ethylacetylene were carried out in a photochemical reaction chamber at one atmosphere of tank air. Reactants and products were monitored via Fourier transform infrared spectroscopy (FTIR) (Digilab 80, Bio Rad Co.). Seventy-two F 40 BLB and twenty-four sun lamps surrounded the 670 liter 9.1 m length 0.31 m diameter borosilicate chamber. The FTIR spectrometer was optically coupled to an adjustable eight mirror multi-pass absorption system within the chamber. A more detailed discussion of the optical system, interferometer, and spectral data techniques are given elsewhere.[2] In these experiments the path length was 144 m and spectral resolution was 1.0 cm^{-1}.

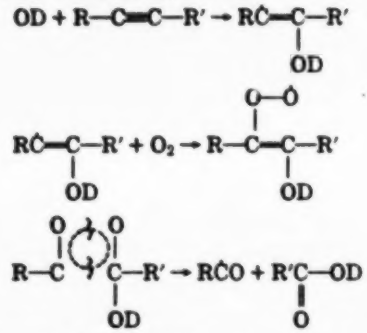
The reactants used were research grade quality and except for acetylene were used without further prepurification. The acetylene was prepurified to remove traces of the acetone stabilizer with a one meter ⅛ inch OD column of Porapak Q in a prep GC operated at 80°C. Zero grade tank air was used which contained less than one ppb oxides of nitrogen.

Five minute irradiation times were used in these experiments. At the end of the five-minute period the reaction progress in the chamber was determined with the FTIR system.

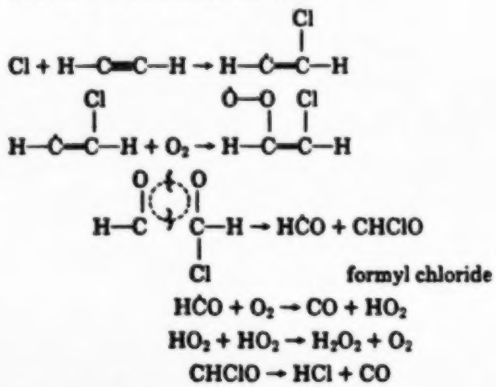
Results and Discussion

Table I shows the ozone yield from the irradiation of acetylene and chlorine in air. The initial chlorine concentration was held constant at 7 ppm and acetylene varied between 17 and 230 ppm. From the table it is observed that for mixtures containing 40 ppm acetylene and above the yield was about 10 percent. Other products observed in the infrared spectra for this system were formyl chloride (CHClO), carbon monoxide (CO), hydrogen chloride (HCl), hydrogen peroxide (H_2O_2) and traces of formic acid (HCOOH). For the range of acetylene shown in Table I, 10 ppm of acetylene had reacted in all irradiation tests and 11 ppm of carbon monoxide was produced. Compounds such as hydrogen chloride, hydrogen peroxide, and formic acid are very susceptible to wall adsorption. Formyl chloride thermally decomposes to HCl and CO.

A reaction mechanism proposed by Hatakeyama et al.[3] for the OD radical reaction with acetylenes involves a four membered ring containing the two acetylene carbons and oxygen (O_2) which added to the carbon directly bonded to the carbon to which OD radical added. This four membered ring splits forming the observed products.



It is proposed that in reaction of acetylene, the chlorine radical acts like OD radical adding to acetylene. Thus the following mechanism can be written:



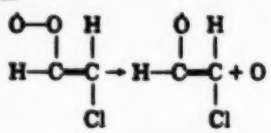
formyl chloride

$$H\dot{C}O + O_2 \rightarrow CO + HO_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$CHClO \rightarrow HCl + CO$$

Ozone formation:



$$O + O_2 \xrightarrow{M} O_3$$

Ozone was not observed in the irradiated systems containing either methylacetylene or ethylacetylene as a substitute for acetylene. Both substituted acetylenes formed formyl chloride as product. Nitrogen dioxide was also added to the

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methylacetylene/chlorine system and irradiated. Upon irradiation the system formed peroxyacetyl nitrate. Similarly, the ethylacetylene/chlorine/nitrogen dioxide system formed peroxypropionyl nitrate. These results are consistent with the formation of formyl chloride from one of the acetylenic carbons and the formation of RĊO radical from the other.

Table I. Ozone yield at five minutes irradiation.

$(C_3H_2)_i$ ppm	Ozone yield
17	.06
40	0.09
75	0.09
100	0.09
130	0.09
230	0.11

$(Cl_2)_i$ = Initial concentration was 7 ppm for all irradiations.

The RĊO radical adds oxygen to form RC(O)OȮ which adds nitrogen dioxide to form peroxyacetyl nitrate or peroxypropionyl nitrate.

Hanst and Calvert[4] postulated the formation of ozone in the photolysis of azomethane and oxygen with added tetramethylethylene. They observed acetone as a product which they stated could only come from the reaction of tetramethylethylene with ozone. No direct spectral evidence however was given for ozone formation. In another study, Niki et al.[5] spectroscopically observed the formation of $^{16}O_3$ in the ozonolysis of trans-1,2-dichloroethylene using labeled $^{18}O_3$. The Creigee intermediate was postulated as being highly energetic, eliminating an atomic oxygen leading to the formation of ozone. Hatakeyma et al.[6] in the photolysis of ketene postulates the reaction of $CH_2 + O_2$ to give $CH_2O + O$. The atomic oxygen reacts with molecular oxygen forming ozone which they observed by its infrared absorption spectra.

In the acetylene/chlorine system we postulate the formation of a energetic peroxy radical formed after the addition of oxygen to the chloroacetylene radical that has the potential to produce atomic oxygen. The elimination of energetic atomic oxygen helps stabilize the remaining species and it reacts with oxygen O_2 in the presence of a third body to form ozone. With substituted acetylenes no ozone was observed in similar chlorine radical reaction systems. Apparently the peroxy radical formed is more electronically stable and cannot eliminate atomic oxygen. However, the proposed mechanism is clearly only consistent with the experimental data. Additional experiments are required to more fully clarify the reaction pathway for O_3 and to determine whether addition of OH can result in O_3 formation in the absence of NO_x.

Disclaimer

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References

1. B. W. Gay, Jr., R. C. Noonan, J. J. Bufalini, P. L. Hanst, "Photochemical synthesis of peroxyacetyl nitrates in gas phase via chlorine-aldehyde reaction," *Environ. Sci. Technol.* 10: 82 (1976).
2. B. W. Gay, Jr., P. L. Hanst, J. J. Bufalini, R. C. Noonan, "Atmospheric oxidation of chlorinated ethylenes," *Environ. Sci. Technol.* 10: 58 (1976).
3. S. Hatakeyama, N. Washida, H. Akimoto, "Rate constants and mechanisms for reaction of OH (OD) radicals with acetylene, propyne, and 2-butyne in air at 297 ± 2K," *J. Phys. Chem.* 90: 173 (1986).
4. P. L. Hanst, J. G. Calvert, "Photolysis of azomethane in air," *J. Phys. Chem.* 63: 71 (1959).
5. H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach, and R. I. Martinez, "Fourier transform infrared study of the gas-phase reaction of $^{18}O_3$ with trans-CHCl—CHCl in $^{16}O_2$-rich mixtures, branching ratio for C- atom production via dissociation of the primary criegee intermediate," *J. Phys. Chem.* 88: 766 (1984).
6. S. Hatakeyama, H. Bandow, M. Okuda, H. Okimoto, "Reactions of CH_2OO and $CH_2(^1A_1)$ with H_2O in the gas phase," *J. Phys. Chem.* 85: 2249 (1981).

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